

## Spotlights on Recent JACS Publications

### ■ PREDICTING DNA RADIATION DAMAGE RATES WITH SPECTROSCOPY AND THEORY

Ionizing radiation can induce oxidative damage to DNA, including double-strand breaks, which can lead to mutations and possibly cancer. To theoretically predict the rate of certain indicators of this damage, researchers need several pieces of information, including the one-electron redox potential of the five nucleobases. However, it has been difficult to measure these properties electrochemically, and other recent approaches have not considered the bases in aqueous solution, their native habitat.

Now Petr Slavíček, Bernd Winter, Pavel Jungwirth, Stephen E. Bradforth, and colleagues have determined the one-electron redox potentials of nucleic acid bases in water with a combined experimental–computational approach (DOI: 10.1021/ja508149e). They use liquid-jet photoelectron spectroscopy to measure the vertical ionization energies of nucleobase components, including purine and pyrimidine nucleotides, nucleosides, pentose sugars, and inorganic phosphate, and then use quantum chemistry calculations to estimate the reorganization energies to the change in nucleobase charge. By combining these two data sets, the authors have determined sufficiently accurate reduction potentials for nucleobases in their native environment, values that could help clarify the rate of oxidative damage to DNA in sunlight and higher-energy sources of radiation.

Deirdre Lockwood, Ph.D.

### ■ ALIOVALENT DOPING IN ITO NANOCRYSTALS LEADS TO BIG SHIFTS

Semiconductor nanocrystals with localized surface plasmon resonance properties have the potential to be useful in technologies such as sensing and imaging. However, while scientists have explored gold and silver nanocrystals, plasmonic oxide nanocrystals have received less attention. The latter constructs have useful properties as well, such as a resonance band in the infrared, and easily tunable bands, which chemists can access by changing the density of doped ions in the lattice.

Here, Daniel Gamelin, Delia Milliron, and co-workers examine two different types of doping in indium tin oxide nanocrystals (DOI: 10.1021/ja5116953). The first involves aliovalent substitution, where the researchers swap out  $\text{Sn}^{4+}$  for  $\text{In}^{3+}$ . They also examine photochemical doping, where they can control the number of electrons they add to the nanocrystals.

The researchers find that the number of electrons they can add to the nanocrystals photochemically is independent of the number of electrons already present from the  $\text{Sn}^{4+}$  doping. This observation suggests that the extra electrons are stabilized by the dopant ions, and that aliovalent doping does not appreciably alter the energy of the electrons in the crystal. The authors conclude that adding impurities to the nanocrystal has significant effects, and these findings may lead to more efficient sensors and imaging technologies in the future.

Leigh Krietsch Boerner, Ph.D.

### ■ NEW HYDROGEN STORAGE MATERIAL CAN TAKE THE HEAT

Hydrogen gas is touted as a possible clean alternative energy source. But without a way to store the gas safely, hydrogen fuel cells will not be practical. For some applications, the stored gas must be stable for long periods of time, sometimes under extreme temperatures. Now, Shih-Yuan Liu and his colleagues have created an  $\text{H}_2$  storage molecule that does not decompose even at temperatures up to 150 °C (DOI: 10.1021/ja511766p).

Amine boranes have relatively high  $\text{H}_2$ -storage capacities and can release the gas quickly, but generally the compounds are not stable at high temperatures. The researchers synthesize the new compound, a bis-BN cyclohexane, in three steps. When dissolved in tetrahydrofuran along with a ruthenium catalyst at room temperature, the compound releases hydrogen in as little as 15 min.

The molecule's storage capacity is 4.7% hydrogen by weight. For use in vehicle fuel cells, the researchers would have to reengineer the compound to increase capacity, since the U.S. Department of Energy has set a 5.5 wt% system target for hydrogen storage for 2020. But the compound may be appropriate for other applications, such as in backup generators that would store energy long term in case of a natural disaster, the authors say.

Leigh Krietsch Boerner, Ph.D., adapted from *Chemical & Engineering News* with permission.

### ■ SCIENTISTS LEARN SOME NEW TRICKS IN THE SHELL GAME

Mineral-making organisms such as coral, crabs, and seashells produce their hard shells in a mysterious process that material scientists are eager to understand and to utilize in the lab. Often, at the heart of this process is the spontaneous conversion of amorphous calcium carbonate to crystalline minerals—aragonite or calcite—or alternatively maintenance of a “frozen” bioavailable amorphous form. Some evidence suggests that water content and the presence of additives, such as phosphate, in amorphous calcium carbonate tune its propensity to crystallize.

Here, Technion and Weizmann Institute researchers use solid state NMR spectroscopy to study the effects of water and phosphate on the transition between amorphous calcium carbonate and calcite (DOI: 10.1021/ja511869g). Examining how increased concentrations of phosphate stabilize amorphous calcium carbonate, they observe that, initially, water and phosphate are homogeneously dispersed in the amorphous calcium carbonate matrix. A simultaneous extraction of water and phosphate is key to the subsequent crystallization; however, too little water relative to phosphate could lock the material in an amorphous state. These details may aid in the development of biomimetic materials for bioengineering or medical applications.

Erika Gebel Berg, Ph.D.

Published: January 21, 2015

## ■ A STABLE RHODIUM $\sigma$ -ALKANE COMPLEX FROM SOLID-STATE SYNTHESIS

Targeted functionalization of simple alkanes, such as methane and ethane, can provide access to high value-added fine chemicals. Although the selective activation of C–H bonds by transition metal catalysts holds the key to this process, the poor nucleophilicity of alkanes often leads to short-lived intermediates, hindering the elucidation of detailed reaction mechanisms.

Using single-crystal to single-crystal transformation, Andrew S. Weller, Stuart A. Macgregor, and co-workers have prepared a highly stable Rh(I)  $\sigma$ -norbornane complex by hydrogenating the crystalline norbornadiene-coordinated precursor (DOI: 10.1021/ja510437p). While X-ray crystallography accurately reveals the structure of this product, especially the hydrogen atoms involved in coordination, NMR spectroscopy and DFT calculations further confirm a three-center, two-electron Rh...H–C  $\sigma$  interaction, where  $\sigma_{\text{CH}} \rightarrow \text{Rh}$  donation plays a dominant role.

The unusual stability of this complex is mainly attributed to its crystal motif, in particular the influence of the phosphine ligand, as similar complexes with structurally related ligands decompose easily. In addition to uncovering a rare yet stable  $\sigma$ -alkane complex, this work offers a new possibility for the synthesis and characterization of such species with various combinations of metals and ligands, which may eventually help clarify modes of C–H activation in alkanes.

**Xin Su**, Ph.D.